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A MECHANICAL MODEL FOR LIQUID NANOLAYERS

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Liquids in contact with solids are submitted to intermolecular forces making liquids heterogeneous and stress tensors are not any more spherical as in homogeneous bulks. The aim of this article is to show that a square-gradient functional representing liquid-vapor interface free energy corrected with a liquid density functional at solid surfaces is a well adapted model to study structures of very thin nanofilms near solid walls. This result makes it possible to study the motions of liquids in nanolayers and to generalize the approximation of lubrication in long wave hypothesis.

Keywords: Nanolayers, disjoining pressure, thin flows, approximation of lubrication.

1. Introduction

At the end of the nineteenth century, the fluid inhomogeneity in liquid-vapor interfaces was taken into account by considering a volume energy depending on space density derivative.[1] This van der Waals square-gradient functional is unable to model repulsive force contributions and misses the dominant damped oscillatory packing structure of liquid interlayers near a substrate wall.[2] Furthermore, the decay lengths are correct only close to the liquid-vapor critical point where the damped oscillatory structure is subdominant.[3] In mean field theory, weighted density-functional has been used to explicitly demonstrate the dominance of this structural contribution in van der Waals thin films and to take into account long-wavelength capillary-wave fluctuations as in papers that renormalize the square-gradient functional to include capillary wave fluctuations.[4] In contrast, fluctuations strongly damp oscillatory structure and it is mainly for this reason that van der Waals' original prediction of a *hyperbolic tangent* is so close to simulations and experiments.[5] The recent development of exper-

imental technics allows us to observe physical phenomena at length scales of a few nanometers.[6] To get an analytic expression in density-functional theory for liquid film of a few nanometer thickness near a solid wall, we add a liquid density-functional at the solid surface to the square-gradient functional representing closely liquid-vapor interface free energy. This kind of functional is well-known in the literature.[7] It was used by Cahn in a phenomenological form, in a well-known paper studying wetting near a critical point.[8] An asymptotic expression is obtained in[9] with an approximation of hard sphere molecules and London potentials for liquid-liquid and solid-liquid interactions: we took into account the power-law behavior which is dominant in a thin liquid film in contact with a solid.
For fluids submitted to this density-functional, we recall the equation of motion and boundary conditions. We point out the definition of disjoining pressure and analyze the consequences of the model. Finally, we study the motions in liquid nanolayers; these motions are always object of many debates. Within lubrication and long wave approximations, a relation between disjoining pressure, viscosity of liquid, nanolayer thickness variations along the layer and tangential velocity of the liquid is deduced.

2. The density-functional

The free energy density-functional of an inhomogeneous fluid in a domain O of boundary ∂O is taken in the form

$$F = \int\int\int_O \varepsilon \, dv + \int\int_{\partial O} \varphi \, ds. \tag{1}$$

The first integral is associated with square-gradient approximation when we introduce a specific free energy of the fluid at a given temperature θ, $\varepsilon = \varepsilon(\rho, \beta)$ as a function of density ρ and $\beta = (\operatorname{grad} \rho)^2$. Specific free energy ε characterizes together fluid properties of *compressibility* and *molecular capillarity* of liquid-vapor interfaces. In accordance with gas kinetic theory, $\lambda = 2\rho\, \varepsilon'_\beta(\rho, \beta)$ is assumed to be constant at given temperature[10] and

$$\rho\, \varepsilon = \rho\, \alpha(\rho) + \frac{\lambda}{2} (\operatorname{grad} \rho)^2, \tag{2}$$

where term $(\lambda/2)\,(\operatorname{grad} \rho)^2$ is added to the volume free energy $\rho\, \alpha(\rho)$ of a compressible fluid. Specific free energy α enables to connect continuously liquid and vapor bulks and pressure $P(\rho) = \rho^2 \alpha'_\rho(\rho)$ is similar to van der Waals one. Near a solid wall, London potentials of liquid-liquid and liquid-

solid interactions are

$$\begin{cases} \varphi_{ll} = -\dfrac{c_{ll}}{r^6}\,, & \text{when } r > \sigma_l \text{ and } \varphi_{ll} = \infty \text{ when } r \le \sigma_l\,, \\ \varphi_{ls} = -\dfrac{c_{ls}}{r^6}\,, & \text{when } r > \delta \text{ and } \varphi_{ls} = \infty \text{ when } r \le \delta\,, \end{cases}$$

where c_{ll} and c_{ls} are two positive constants associated with Hamaker constants, σ_l and σ_s denote fluid and solid molecular diameters, $\delta = \frac{1}{2}(\sigma_l + \sigma_s)$ is the minimal distance between centers of fluid and solid molecules.[11] Forces between liquid and solid have short range and can be described simply by adding a special energy at the surface. This is not the entire interfacial energy: another contribution comes from the distortions in the density profile near the wall.[9,12] For a plane solid wall (at a molecular scale), this surface free energy is

$$\phi(\rho) = -\gamma_1 \rho + \frac{1}{2}\,\gamma_2\,\rho^2. \tag{3}$$

Here ρ denotes the fluid density value at the wall; constants γ_1, γ_2 are positive and given by relations $\gamma_1 = \dfrac{\pi c_{ls}}{12\delta^2 m_l m_s}\,\rho_{sol}$, $\gamma_2 = \dfrac{\pi c_{ll}}{12\delta^2 m_l^2}$, where m_l and m_s denote respectively masses of fluid and solid molecules, ρ_{sol} is the solid density.[9] Moreover, we have $\lambda = \dfrac{2\pi c_{ll}}{3\sigma_l\, m_l^2}$.

We consider a horizontal plane liquid interlayer contiguous to its vapor bulk and in contact with a plane solid wall (S); the z-axis is perpendicular to the solid surface. The liquid film thickness is denoted by h. Conditions in vapor bulk yield $\operatorname{grad}\rho = 0$ and $\Delta\rho = 0$. Another way to take into account the vapor bulk contiguous to the liquid interlayer is to compute a density-functional of the complete *liquid-vapor interlayer* by adding a supplementary surface energy ψ on a geometrical surface (Σ) at $z = h$ to volume energy (2) in liquid interlayer (L) and surface energy (3) on solid wall (S).[13] This assumption corresponds to a liquid interlayer included between $z = 0$ and $z = h$, a liquid-vapor interface of a few Angström thickness assimilated to surface $z = h$ and a vapor layer included between $z = h$ and $z = \infty$. Due to small vapor density, let us denote by ψ the surface free energy of a liquid in contact with a vacuum,

$$\psi(\rho) = \frac{\gamma_4}{2}\,\rho^2 \tag{4}$$

where $\gamma_4 \simeq \gamma_2$ and ρ is the liquid density in a convenient point inside the liquid-vapor interface.[13] Density-functional (1) of the liquid-vapor layer gets the final form

$$F = \int\int\int_{(L)} \varepsilon\; dv + \int\int_{(S)} \phi\; ds + \int\int_{(\Sigma)} \psi\; ds$$

3. Equation of motion and boundary conditions

In case of equilibrium, functional F is minimal and yields the equation of equilibrium and boundary conditions. In case of motions we simply add the inertial forces $\rho\,\mathbf{\Gamma}$ and the dissipative stresses to the results.[14–16]

3.1. *Equation of motion*

The equation of motion is[14,15]

$$\rho\ \mathbf{\Gamma} = \mathrm{div}\,(\sigma + \sigma_v) - \rho\ \mathrm{grad}\ \Omega\ , \tag{5}$$

where $\mathbf{\Gamma}$ is the acceleration, Ω the body force potential and σ the stress tensor generalization

$$\sigma = -\,p\,\mathbf{1} - \lambda\ \mathrm{grad}\ \rho\ \otimes\ \mathrm{grad}\ \rho,$$

with $p = \rho^2\varepsilon'_\rho - \rho\ \mathrm{div}\ (\lambda\ \mathrm{grad}\ \rho)$. The viscous stress tensor is $\sigma_v = \kappa_1(\ \mathrm{tr}\ D)\,\mathbf{1} + 2\,\kappa_2\ D$ where D denotes the velocity strain tensor; κ_1 and κ_2 are the coefficients of viscosity.
For a horizontal layer, in an orthogonal system of coordinates such that the third coordinate is the vertical direction, the stress tensor σ of the thin film takes the form :

$$\sigma = \begin{bmatrix} a_1,\ 0,\ 0 \\ 0,\ a_2,\ 0 \\ 0,\ 0,\ a_3 \end{bmatrix}, \quad \text{with} \quad \begin{cases} a_1 = a_2 = -P + \dfrac{\lambda}{2}\left(\dfrac{d\rho}{dz}\right)^2 + \lambda\,\rho\,\dfrac{d^2\rho}{dz^2} \\ a_3 = -P - \dfrac{\lambda}{2}\left(\dfrac{d\rho}{dz}\right)^2 + \lambda\,\rho\,\dfrac{d^2\rho}{dz^2} \end{cases}$$

Let us consider a thin film of liquid at equilibrium (*gravity forces are neglected* but the variable of position is the ascendant vertical). The equation of equilibrium is :

$$\mathrm{div}\ \sigma = \mathbf{0} \tag{6}$$

Eq. (6) yields a constant value for the eigenvalue a_3,

$$P + \frac{\lambda}{2}\left(\frac{d\rho}{dz}\right)^2 - \lambda\rho\,\frac{d^2\rho}{dz^2} = P_{v_b}.$$

where P_{v_b} denotes pressure $P(\rho_{v_b})$ in the vapor bulk of density ρ_{v_b} bounding the liquid layer. Eigenvalues a_1, a_2 are not constant but depend on the distance z to the solid wall.[17] At equilibrium, Eq. (5) yields:[14]

$$\mathrm{grad}\ [\ \mu\,(\rho) - \lambda\Delta\rho\ ] = 0, \tag{7}$$

where μ is the chemical potential at temperature θ defined to an unknown additive constant. The chemical potential is a function of P (and θ) but it

can be also expressed as a function of ρ (and θ). We choose as *reference chemical potential* $\mu_o = \mu_o(\rho)$ null for bulks of densities ρ_l and ρ_v of phase equilibrium. Due to Maxwell rule, the volume free energy associated with μ_o is $g_o(\rho) - P_o$ where $P_o = P(\rho_l) = P(\rho_v)$ is the bulk pressure and $g_o(\rho) = \int_{\rho_v}^{\rho} \mu_o(\rho)\, d\rho$ is null for liquid and vapor bulks of phase equilibrium. The pressure P is

$$P(\rho) = \rho\, \mu_o(\rho) - g_o(\rho) \ + P_o. \tag{8}$$

Thanks to Eq. (7), we obtain in the fluid *and not only in the fluid interlayer,*

$$\mu_o(\rho) - \lambda \Delta\rho = \mu_o(\rho_b),$$

where $\mu_o(\rho_b)$ is the chemical potential value of a liquid *mother* bulk of density ρ_b such that $\mu_o(\rho_b) = \mu_o(\rho_{v_b})$, where ρ_{v_b} is the density of the vapor *mother* bulk bounding the layer. We must emphasis that $P(\rho_b)$ and $P(\rho_{v_b})$ are unequal as for drop or bubble bulk pressures. Density ρ_b is not a fluid density in the interlayer but density in the liquid bulk from which the interface layer can extend (this is the reason why Derjaguin used the term *mother liquid*,[17] *page 32*). In the interlayer

$$\lambda \frac{d^2\rho}{dz^2} = \mu_b(\rho), \quad \text{with} \quad \mu_b(\rho) = \mu_o(\rho) - \mu_o(\rho_b) \tag{9}$$

3.2. *Boundary conditions*

Condition at the solid wall (S) is associated with Eq. (3)[15] :

$$\lambda \left(\frac{d\rho}{dn}\right)_{|S} + \phi'(\rho)_{|S} \ = 0, \tag{10}$$

where n is the external normal direction to the fluid; Eq. (10) yields

$$\lambda \left(\frac{d\rho}{dz}\right)_{|z=0} = -\gamma_1 + \gamma_2 \ \rho_{|z=0}.$$

Condition at the liquid-vapor interface (Σ) is associated with Eq. (4):

$$\lambda \left(\frac{d\rho}{dz}\right)_{|z=h} = -\gamma_4 \ \rho_{|z=h}\,. \tag{11}$$

Eq. (11) defines the film thickness by introducing a reference point inside the liquid-vapor interface bordering the liquid interlayer with a convenient density at $z = h$.[13]

We must also add the classical surface conditions on the stress vector associated with the total stress tensor $\sigma + \sigma_v$ to these conditions on density.

4. The disjoining pressure for horizontal liquid films

We consider fluids and solids *at a given temperature* θ. The hydrostatic pressure in a thin liquid interlayer included between a solid wall and a vapor bulk differs from the pressure in the contiguous liquid phase. At equilibrium, the additional pressure interlayer is called the *disjoining pressure*.[17] The measure of a disjoining pressure is either the additional pressure on the surface or the drop in the pressure within the *mother bulks* that produce the interlayer. The disjoining pressure is equal to the difference between the pressure P_{v_b} on the interfacial surface (pressure of the vapor mother bulk of density ρ_{v_b}) and the pressure P_b in the liquid mother bulk (density ρ_b) from which the interlayer extends :

$$\Pi(h) = P_{v_b} - P_b.$$

If $g_b(\rho) = g_o(\rho) - g_o(\rho_b) - \mu_o(\rho_b)(\rho - \rho_b)$ denotes the primitive of $\mu_b(\rho)$ null for ρ_b, we get from Eq. (8)

$$\Pi(\rho_b) = -g_b(\rho_{v_b}), \tag{12}$$

and an integration of Eq. (9) yields

$$\frac{\lambda}{2}\left(\frac{d\rho}{dz}\right)^2 = g_b(\rho) + \Pi(\rho_b). \tag{13}$$

The reference chemical potential linearized near ρ_l (*respectively* ρ_v) is $\mu_o(\rho) = \dfrac{c_l^2}{\rho_l}(\rho - \rho_l)$ (*respectively* $\mu_o(\rho) = \dfrac{c_v^2}{\rho_v}(\rho - \rho_v)$) where c_l (*respectively* c_v) is the isothermal sound velocity in liquid bulk ρ_l (*respectively vapor bulk* ρ_v) at temperature θ.[18] In the liquid and vapor parts of the liquid-vapor film, Eq. (9) yields

$$\lambda\frac{d^2\rho}{dz^2} = \frac{c_l^2}{\rho_l}(\rho - \rho_b) \quad \text{(liquid)} \quad \text{and} \quad \lambda\frac{d^2\rho}{dz^2} = \frac{c_v^2}{\rho_v}(\rho - \rho_{v_b}) \quad \text{(vapor)}.$$

The values of $\mu_o(\rho)$ are equal for the mother densities ρ_{v_b} and ρ_b,

$$\frac{c_l^2}{\rho_l}(\rho_b - \rho_l) = \mu_o(\rho_b) = \mu_o(\rho_{v_b}) = \frac{c_v^2}{\rho_v}(\rho_{v_b} - \rho_v), \quad \text{and consequently,}$$

$$\rho_{v_b} = \rho_v\left(1 + \frac{c_l^2}{c_v^2}\frac{(\rho_b - \rho_l)}{\rho_l}\right).$$

In liquid and vapor parts of the liquid-vapor interlayer we have,

$$g_o(\rho) = \frac{c_l^2}{2\rho_l}(\rho - \rho_l)^2 \quad \text{(liquid)} \quad \text{and} \quad g_o(\rho) = \frac{c_v^2}{2\rho_v}(\rho - \rho_v)^2 \quad \text{(vapor)}.$$

From definition of $g_b(\rho)$ and Eq. (12) we deduce the disjoining pressure

$$\Pi(\rho_b) = \frac{c_l^2}{2\rho_l}(\rho_l - \rho_b)\left[\rho_l + \rho_b - \rho_v\left(2 + \frac{c_l^2}{c_v^2}\frac{(\rho_b - \rho_l)}{\rho_l}\right)\right]. \qquad (14)$$

Due to $\rho_v\left(2 + \frac{c_l^2}{c_v^2}\frac{(\rho_b - \rho_l)}{\rho_l}\right) \ll \rho_l + \rho_b$, we get $\Pi(\rho_b) \approx \frac{c_l^2}{2\rho_l}(\rho_l^2 - \rho_b^2)$.
Now, we consider a film of thickness h; the density profile in the liquid part of the liquid-vapor film is solution of system :

$$\begin{cases} \lambda\dfrac{d^2\rho}{dz^2} = \dfrac{c_l^2}{\rho_l}(\rho - \rho_b) & (S1) \\ \text{with} \quad \lambda\dfrac{d\rho}{dz}_{|z=0} = -\gamma_1 + \gamma_2\ \rho_{|z=0} \quad \text{and} \quad \lambda\dfrac{d\rho}{dz}_{|z=h} = -\gamma_4\ \rho_{|z=h}\,. \end{cases}$$

Quantity τ is defined such that $\tau = c_l/\sqrt{\lambda\rho_l}$, where $1/\tau$ is a reference length and $\gamma_3 = \lambda\tau$. Solution of system $(S1)$ is

$$\rho = \rho_b + \rho_1\, e^{-\tau z} + \rho_2\, e^{\tau z} \qquad (15)$$

where boundary conditions at $z = 0$ and h yield the values of ρ_1 and ρ_2 :

$$\begin{cases} (\gamma_2 + \gamma_3)\rho_1 + (\gamma_2 - \gamma_3)\rho_2 = \gamma_1 - \gamma_2\rho_b & (S2) \\ -e^{-h\tau}(\gamma_3 - \gamma_4)\rho_1 + e^{h\tau}(\gamma_3 + \gamma_4)\rho_2 = -\gamma_4\rho_b. \end{cases}$$

The liquid density profile is a consequence of Eq. (15) when $z \in [0, h]$. Taking Eq. (15) into account in Eq. (13) and $g_b(\rho) = (c_l^2/2\,\rho_l)(\rho - \rho_b)^2$ in linearized form for the liquid part of the interlayer, we get

$$\Pi(\rho_b) = -\frac{2\,c_l^2}{\rho_l}\,\rho_1\,\rho_2. \qquad (16)$$

By identification of expressions (14), (16) and using $(S2)$, we get a relation between h and ρ_b. We denote finally the disjoining pressure by $\Pi(h)$.
Due to the fact that $\rho_b \simeq \rho_l$,[17] the disjoining pressure reduces to

$$\Pi(h) = \frac{2\,c_l^2}{\rho_l}\left[(\gamma_1 - \gamma_2\rho_l)(\gamma_3 + \gamma_4)e^{h\tau} + (\gamma_2 - \gamma_3)\gamma_4\rho_l\right] \times \frac{\left[(\gamma_2 + \gamma_3)\gamma_4\rho_l - (\gamma_1 - \gamma_2\rho_l)(\gamma_3 - \gamma_4)e^{-h\tau}\right]}{\left[(\gamma_2 + \gamma_3)(\gamma_3 + \gamma_4)e^{h\tau} + (\gamma_3 - \gamma_4)(\gamma_2 - \gamma_3)e^{-h\tau}\right]^2}.$$

Let us notice an important property of mixture of van der Waals fluid and perfect gas where the total pressure is the sum of partial pressures of components:[18] at equilibrium, the partial pressure of the perfect gas is constant through the liquid-vapor-gas interlayer -where the perfect gas is dissolved in the liquid. The disjoining pressure of the mixture is the same than for a single van der Waals fluid and calculations and results are identical to those previously obtained.

5. Motions along a liquid nanolayer

When the liquid layer thickness is small with respect to transverse dimensions of the wall, it is possible to simplify the Navier-Stokes equation which governs the flow of a classical viscous fluid in the approximation of lubrication.[19] When $h \ll L$, where L is the wall transversal characteristic size, *i)* the velocity component along the wall is large with respect to the normal velocity component which can be neglected ; *ii)* the velocity vector varies mainly along the direction orthogonal to the wall and it is possible to neglect velocity derivatives with respect to coordinates along the wall compared to the normal derivative ; *iii)* the pressure is constant in the direction normal to the wall. It is possible to neglect the inertial term when $Re \ll L/h$ (Re is the Reynolds number of the flow). Equation of Navier-Stokes is not valid in a liquid nanolayer because the fluid is strongly inhomogeneous and the elastic stress tensor is not scalar. However, it is possible to adapt the approximation of lubrication for viscous flows in a liquid nanolayer. We are in the case of long wave approximation: $\epsilon = h/L \ll 1$. We denote the velocity by $\mathbf{V} = (u, v, w)$ where (u, v) are the tangential components. In the approximation of lubrication we have : $e = \sup(|w/u|, |w/v|) \ll 1$. The main parts of terms associated with second derivatives of liquid velocity components correspond to $\partial^2 u/\partial z^2$ and $\partial^2 v/\partial z^2$. The density is constant along each stream line ($\dot{\rho} = 0 \Longleftrightarrow div\mathbf{V} = 0$) and iso-density surfaces contain the trajectories. Then, $\partial u/\partial x, \partial v/\partial y$ and $\partial w/\partial z$ have the same order of magnitude and $\epsilon \sim e$. As in Rocard model, we assume that the kinematic viscosity coefficient $\nu = \kappa_2/\rho$ depends only on the temperature.[10] In motion equation, the viscosity term is $(1/\rho)$ div $\sigma_v = 2\nu\ [\ \text{div}\ D + D\ \text{grad}\ \{\,\text{Ln}\,(2\,\kappa_2)\}\ ]$; D grad$\{$Ln $(2\,\kappa_2)\}$ is negligible with respect to div D. In both lubrication and long wave approximations the liquid nanolayer motion verifies

$$\mathbf{\Gamma} + \text{grad}[\,\mu_o(\rho) - \lambda\,\Delta\rho\,] = \nu\,\Delta\mathbf{V} \quad \text{with} \quad \Delta\mathbf{V} \simeq \left[\ \frac{\partial^2 u}{\partial z^2},\ \frac{\partial^2 v}{\partial z^2}, 0\right] \qquad (17)$$

In approximation of lubrication, the inertial term is neglected and Eq. (17) separates into tangential and normal components to the solid wall. As in equilibrium, the normal component of Eq. (17) is

$$\frac{\partial}{\partial z}\,[\ \mu_o(\rho) - \lambda\,\Delta\rho\,] = 0 \quad \Rightarrow \quad \mu_o(\rho) - \lambda\,\Delta\rho = \mu_o(\rho_b).$$

To each value ρ_b (different of liquid bulk density value ρ_l of the plane interface at equilibrium) is associated a liquid nanolayer thickness h. We can write $\mu_o(\rho) - \lambda\,\Delta\rho = \eta(h)$, where η is such that $\eta(h) = \mu_o(\rho_b)$. For

one-dimensional motions colinear to the solid wall (direction $\mathbf{i_o}$ and velocity $u\,\mathbf{i_o}$), the tangential component of Eq. (17) yields :

$$\text{grad}\ \mu_o(\rho_b) = \nu \frac{\partial^2 u}{\partial z^2}\ \mathbf{i_o} \quad \Longleftrightarrow \quad \frac{\partial \mu_o}{\partial \rho_b}\ \frac{\partial \rho_b}{\partial x} = \ \nu \frac{\partial^2 u}{\partial z^2}. \tag{18}$$

A liquid can slip on a solid wall only at a molecular level.[20] The sizes of solid walls are several orders of magnitude higher than slipping distances which are negligible and kinematic condition at solid walls is the adherence condition ($z = 0 \ \Rightarrow \ u = 0$). From the continuity of fluid tangential stresses through a liquid-vapor interface of molecular size and assuming that vapor viscosity stresses are negligible, we obtain ($z = h, \ \Rightarrow \ \dfrac{\partial u}{\partial z} = 0$). Consequently Eq. (18) implies $\nu\, u = \dfrac{\partial \mu_o}{\partial \rho_b}\ \dfrac{\partial \rho_b}{\partial x}\ \left(\dfrac{1}{2}\, z^2 - h\, z\right)$. The mean spatial velocity $\overline{u}$ of the liquid in the nanolayer is $\overline{u} = \frac{1}{h}\int_o^h u\ dz$; previous computations yield $\nu\ \overline{\mathbf{u}} = -\dfrac{h^2}{3}\ \text{grad}\ \mu_o(\rho_b)$ with $\overline{\mathbf{u}} = \overline{u}\ \mathbf{i_o}$. Let us remark that

$$\frac{\partial \mu_o(\rho_b)}{\partial x} = \frac{\partial \mu_o}{\partial \rho_b}\ \frac{\partial \rho_b}{\partial h}\ \frac{\partial h}{\partial x} \equiv \frac{1}{\rho_b}\ \frac{\partial P(\rho_b)}{\partial \rho}\ \frac{\partial \rho_b}{\partial h}\ \frac{\partial h}{\partial x}.$$

The pressure P_{v_b} in the vapor bulk is constant along flow motions and $\Pi(h) = P_{v_b} - P(\rho_b)$; consequently, we get $\dfrac{\partial \mu_o(\rho_b)}{\partial x} = -\dfrac{1}{\rho_b}\ \dfrac{\partial \Pi(h)}{\partial h}\ \dfrac{\partial h}{\partial x}$ and

$$\chi_b\ \overline{\mathbf{u}} = \frac{h^2}{3}\ \text{grad}\ \Pi(h). \tag{19}$$

where $\chi_b = \rho_b \nu$ is the liquid kinetic viscosity.

Eq. (19) yields the mean spatial velocity of the isothermal liquid nanolayer as a function of the disjoining pressure gradient. Like as the disjoining pressure depends on the nanolayer thickness, the mean flow velocity is a function of thickness variations along the flow.

Taking into account that in the liquid nanolayer $\rho \simeq \rho_b$, then

$$\left(\int_o^h \rho\ dz\right)\ \overline{\mathbf{u}} \simeq \int_o^h \rho\, \mathbf{u}\ dz$$

and the mean spatial velocity corresponds also to the mean velocity with respect to the mass density.

In shallow water approximation, the equation of continuity yields

$$\frac{\partial}{\partial t}\left(\int_o^h \rho\ dz\right) + \text{div}\left\{\left(\int_o^h \rho\ dz\right)\overline{\mathbf{u}}\right\} = 0$$

and we obtain Eq. (14) in ref. ([21]) associated with $h-$perturbations :

$$\frac{\partial h}{\partial t} + h \ \mathrm{div}\overline{\mathbf{u}} = 0.$$

Thanks to Eq. (19) an equation for $h-$perturbations is :

$$\frac{\partial h}{\partial t} + \frac{h}{3\,\chi_b}\,\frac{\partial}{\partial x}\left(h^2 \frac{\partial}{\partial x}\Pi(h)\right) = 0. \tag{20}$$

Eq. (20) is an *equation of diffusion* in parabolic structure with a good sign of diffusion coefficient associated with stability when $\dfrac{\partial \Pi(h)}{\partial h} < 0$.[17]

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